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Electrochemical Oxidation of Metal Carbides in Aqueous Solutions

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Transition metal carbides have unique properties such as high hardness, high melting temperatures, high thermal conductivity, and high chemical stability. In this report, we investigate the electrochemical oxidation of a series of metal carbides including NbC, Nb₂C, TaC, Ta₂C, VC, VCrC, TiC and TiCrC in neutral, basic, or acidic aqueous solutions. Cyclic voltammetry and elemental analysis demonstrated that many of these metal carbides can be electrochemically oxidized at low electrode potentials to produce soluble metal ions in the solutions. Carbon in the metal carbides remains on the electrode substrates and forms porous carbide-derived carbon (CDC). The surface morphology of the CDC and specific surface area depend on the metal carbide precursors and the electrochemical oxidation conditions.

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Transition metal carbides have extensive applications in many areas of the chemical and mechanical industries.^{1,2} For example, the refractory and hard ceramic material niobium carbides (NbC and Nb₂C) have been broadly used as coatings for cutting tool bits and to improve wear resistance. Several transition metal carbides resemble the valence electron structures and the catalytic properties of metals such as Pt and Pd.²⁻⁵ The metal carbides or the Carbide-Derived Carbon (CDC) obtained from these metal carbide precursors can be used as supports to reduce the overall loading of the precious metals.^{6,7} Pt nanoparticles demonstrate superior catalytic effects when they are loaded on WC or W₂C powders for many reactions such as hydrogen oxidation, hydrogen evolution, alcohol oxidation, and oxygen reduction reactions.⁸

Due to their chemical stability and poor sintering ability, research on the chemical properties of the metal carbides is restricted to limited areas.^{1,9} Metal carbides can be oxidized at higher temperatures with different oxidants. For example, NbC powder can be oxidized in an oxygen atmosphere at 420–600°C to produce Nb₂O₅.¹⁰ At a temperature of 350°C or higher, most carbides can react with chlorine gas to form volatile metal chloride (MCl₄). The left-over porous CDC is metal free and sp² or sp³ hybridized.^{11,12} At room temperature, metal carbides are very stable in strong acidic solutions. However, when an electrical potential is applied, metal carbides can also be oxidized to form metal oxides.^{3,13} In addition to the binary metal carbides, MAX phase metal carbides (Ti₃AlC₂, Ti₂AlC and Ti₃SiC₂) can be oxidized in acidic electrolyte solutions (HCl and HF) by electrochemical etching and yield CDC with uniformly distributed nanoscale pores.^{14,15} In a previous report, binary metal carbides (VC and V₂C) were electrochemically etched in acidic, neutral, or basic aqueous solutions and produced CDC materials that were excellent electrode materials for electronic double layer supercapacitors.¹⁶

In this paper, we investigate the electrochemical properties of a series of metal carbides, NbC, Nb₂C, TaC, Ta₂C, VC, VCrC, TiC and TiCrC in aqueous solutions with the presence of HCl, HF, KCl, or NaOH. Cyclic voltammetry and elemental analysis demonstrated that several carbides can be oxidized electrochemically at “mild” electrode potentials and produce soluble metal ions in the solutions. The remaining carbon atoms on the surface of the electrode after oxidation might be sp³ or sp² hybridized, indicating the existence of the CDC structure.

Materials and Methods

Binary carbide precursors were synthesized using a reactive magnetron sputtering approach in a partial pressure of methane at elevated temperatures on various substrates as described previously.¹⁶ X-ray diffraction (XRD) was used to confirm the phase of the material synthesized. The different phases were obtained by changing the methane partial pressure used during sputter deposition.

Cyclic Voltammetry was carried out using an Autolab 302N Potentiostat. The metal carbide coated substrates were used directly as the working electrodes in the electrochemical measurements. The working electrodes were mounted in a plastic electrochemical cell with an exposed area of 0.44 cm². A coiled Pt-wire counter electrode and an Ag/AgCl reference electrode were used for all of the measurements. Only representative CVs obtained from each metal carbide are shown in the figures.

The microstructures of the coatings were investigated post-treatment using a LEO 1530 VP scanning electron microscope (SEM). Raman spectroscopy measurements were performed using a Horiba LabRam HR Raman Spectrometer with 600/mm and 1800/mm gratings and a confocal microscope with a mapping stage. A green 532nm laser beam incident on the surface of the CDC film was focused to a spot size of approximately 0.30 mm diameter. Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) measurements were performed using an Agilent 7500 ICP-MS equipped with an Ar ICP torch and a single quadrupole mass analyzer. Metal standard solutions in 2% HNO₃ were purchased from Buck Scientific Inc. and diluted to the desired concentration prior to the ICP-MS measurements. These standard solutions and the specified dilutions were measured in series with the solutions used to etch the carbides.

Results and Discussion

Structure characterization of metal carbides.—The results of XRD measurements for the materials discussed in this paper are presented in Figure 1. The cubic phases are highly textured and possibly epitaxial on the Al₂O₃ substrates dominated by the (111) peaks as labeled in the plots. The hexagonal phases are also very textured with (002) peaks dominating the pattern and a noticeable (011) peak (typically the largest peak in a powder diffraction measurement) observed in all the hexagonal materials. The highly textured nature of the coatings indicated by the XRD peaks suggest that the coatings are very dense and uniform. The shift in the (111) peaks in TiC and VCrC suggest that the coatings are strained likely due to a lattice mismatch

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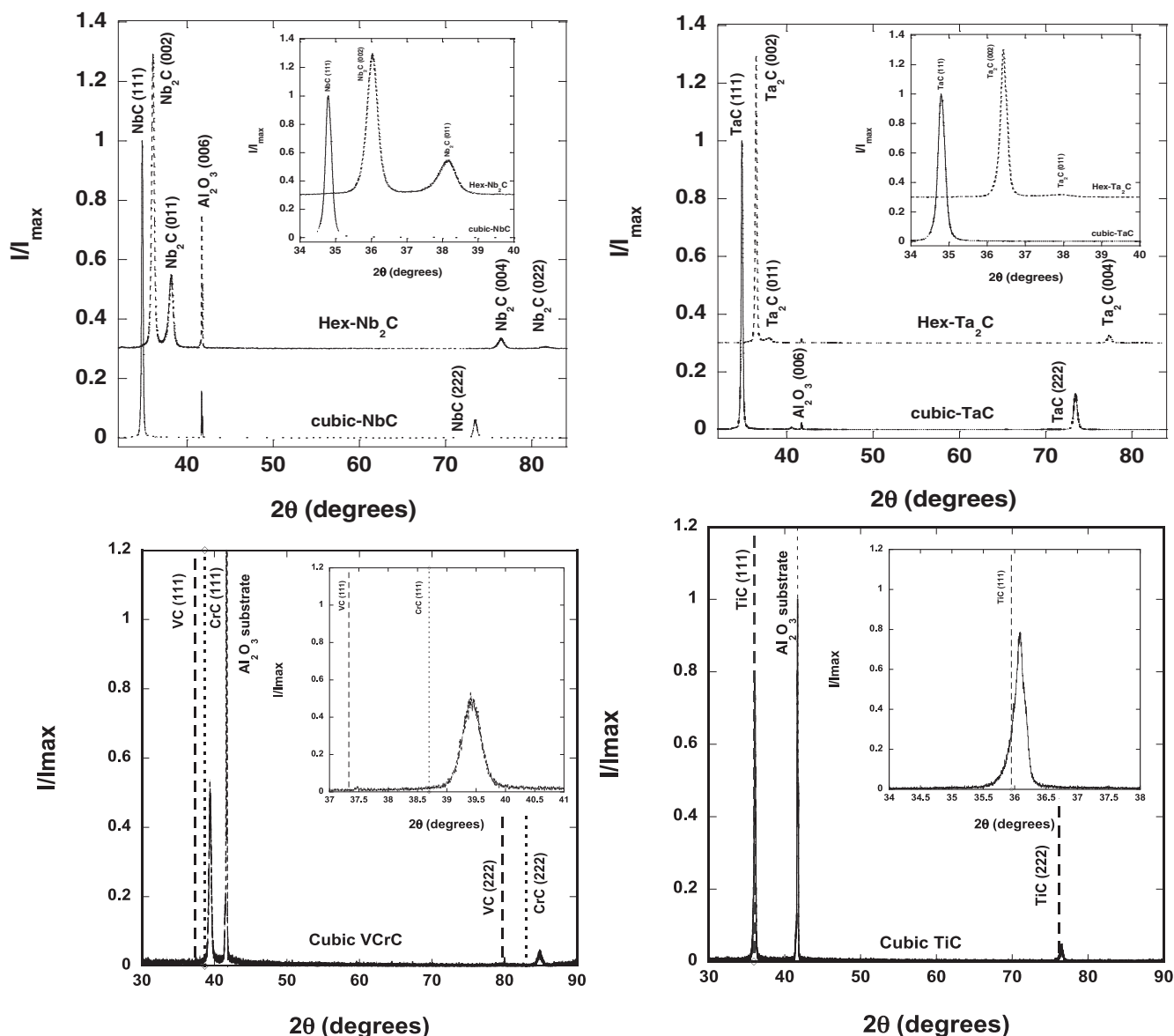


Figure 1. XRD measurements of NbC, Nb₂C, TaC, Ta₂C, VCrC, and TiC films. The observation of the (111) and (222) peaks indicate a strong texturing of the crystallites in these coatings. The dashed lines in the figures show the locations of the peaks in VC, VCrC and TiC according to a powder diffraction file database. The shift of the peaks (enlarged in the insets) suggest that there is significant strain in the coatings.

with the Al₂O₃ substrate. The TiCrC XRD result is not shown. The film was deposited on silicon and is not epitaxial. The XRD peaks are very small indicating very small crystallites.

Electrochemical oxidation of niobium carbides.—Metal carbides have very low resistivity (<300 μΩcm) and, therefore, can be used as a working electrode directly in an electrochemical setup regardless of whether the substrate is an electrical conductor or insulating material.¹⁷ Figures 2A–2F shows the cyclic voltammograms (CV) of NbC and Nb₂C obtained in neutral (0.1 M KCl), acidic (1.0 M HCl), and basic (0.2 M NaOH) solutions, starting with a positive scan up to 1.2 V vs. Ag/AgCl. In each situation, after a critical potential is reached, an ever-increasing oxidation current is observed indicating the oxidation of the carbides. For NbC, this critical potential is about 0.9 V in HCl, 0.7 V in KCl, and 0.3 V in NaOH; while for Nb₂C, this critical potential is about 0.6 V in HCl, 0.4 V in KCl, and 0.2 V in NaOH. Qualitatively, these observations can be summarized by stating that the oxidation of Nb₂C is “easier” and showed a significantly larger oxidation profile in the CV curves. For both NbC and

Nb₂C, the oxidation potentials are the lowest in NaOH and the highest in HCl. In general, the carbides are more easily oxidized in a basic solution when compared to neutral or acidic solutions. The oxidation current decreased significantly after the second scan and stabilized after tens of scans (exact numbers depend on the electrolyte solutions and other parameters of the potential sweep). The two hundredth scans of the CV are shown in Figure 2 and demonstrate very small values of faradaic current, which would indicate limited electron-transfer reactions. In contrast, in a previous paper, we reported the observation of an increase in the non-faradaic current, indicating an increase of surface area and double layer capacitance when vanadium carbides were oxidized in all of these electrolyte solutions.¹⁶ However, this larger specific surface area or double layer capacitance is not observed when NbC or Nb₂C are oxidized.

It has been demonstrated that the addition of HF in the electrolyte solution significantly affected the oxidation of MAX phase metal carbides.¹⁵ In our experiments, the HF (concentrations from 0.001 M to 0.1 M) did not significantly affect the first cycle of the NbC oxidation as is shown in Figure 3A. The oxidation potentials

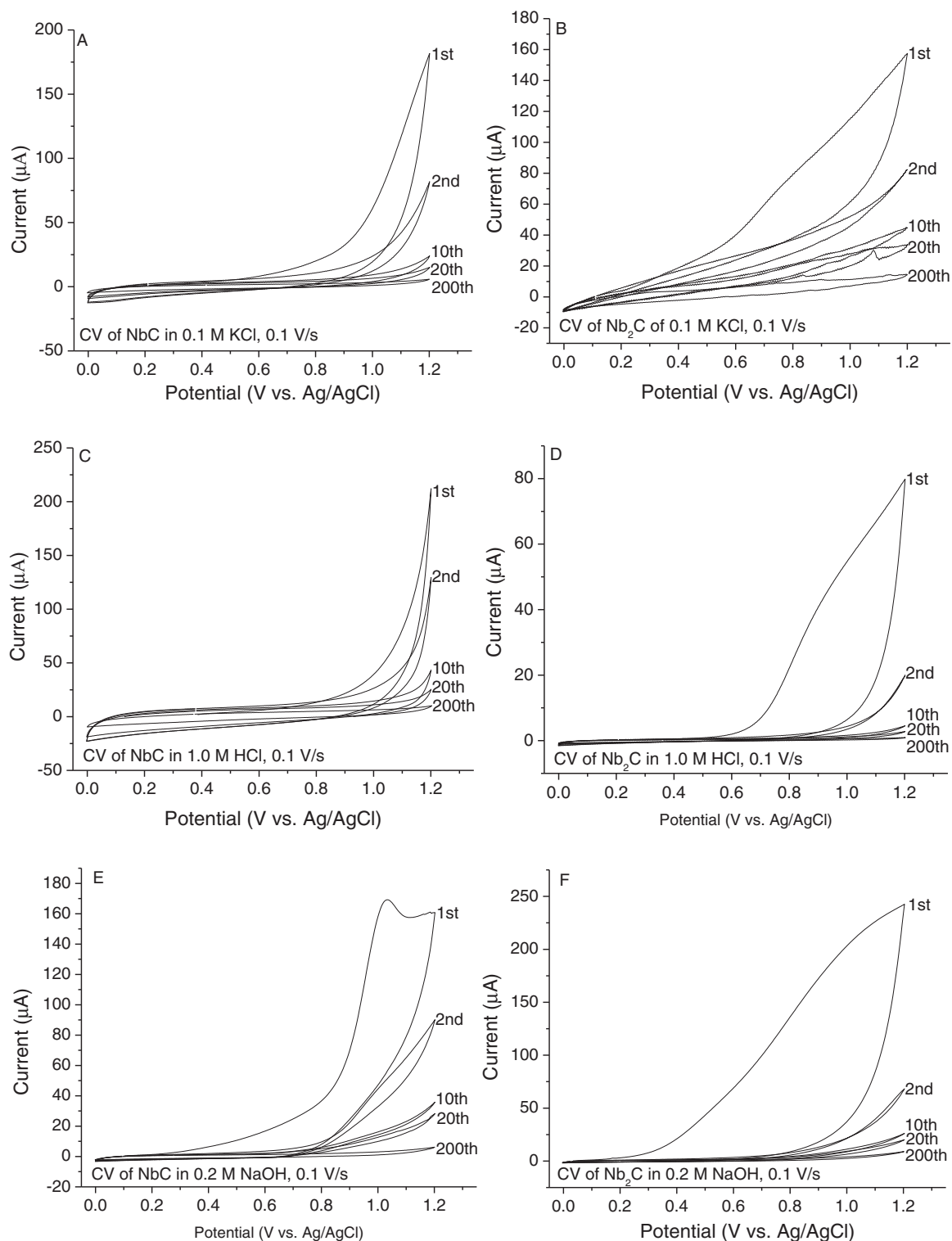


Figure 2. CVs for NbC (A, C, and E) and Nb₂C (B, D, and F) electrodes in 0.1 M KCl (A and B), 1.0 M HCl (C and D), and 0.2 M NaOH (E and F) solutions at a scan rate of 0.1 V/s. The first, second, tenth, twentieth, and two hundredth scans are shown.

and currents are very close in electrolyte solutions containing HF in concentrations varied from 0.001 M to 0.1 M. After 200 scans, the residual current is larger when HF is present in the solutions as shown in Figure 3B. In the case of Nb₂C, an appreciable concentration of HF (0.1 M) will lower the oxidation potential and significantly increase the residual current after 200 cycles as shown in Figures 3C and 3D.

After electrochemical oxidation, Nb can be detected in the electrolyte solutions. Table I shows the Nb concentrations, measured by ICP-MS, in different electrolyte solutions after 200 scans. It can be seen that, for both NbC and Nb₂C, the Nb concentration in electrolyte solutions increased when the solution is changed from 0.1 M KCl to 1.0 M HCl, 1.0 M HCl with 0.001 M HF, 1.0 M HCl with 0.01 M HF, and 1.0 M HCl with 0.1 M HF in turn. In the mixture of 1.0 M HCl

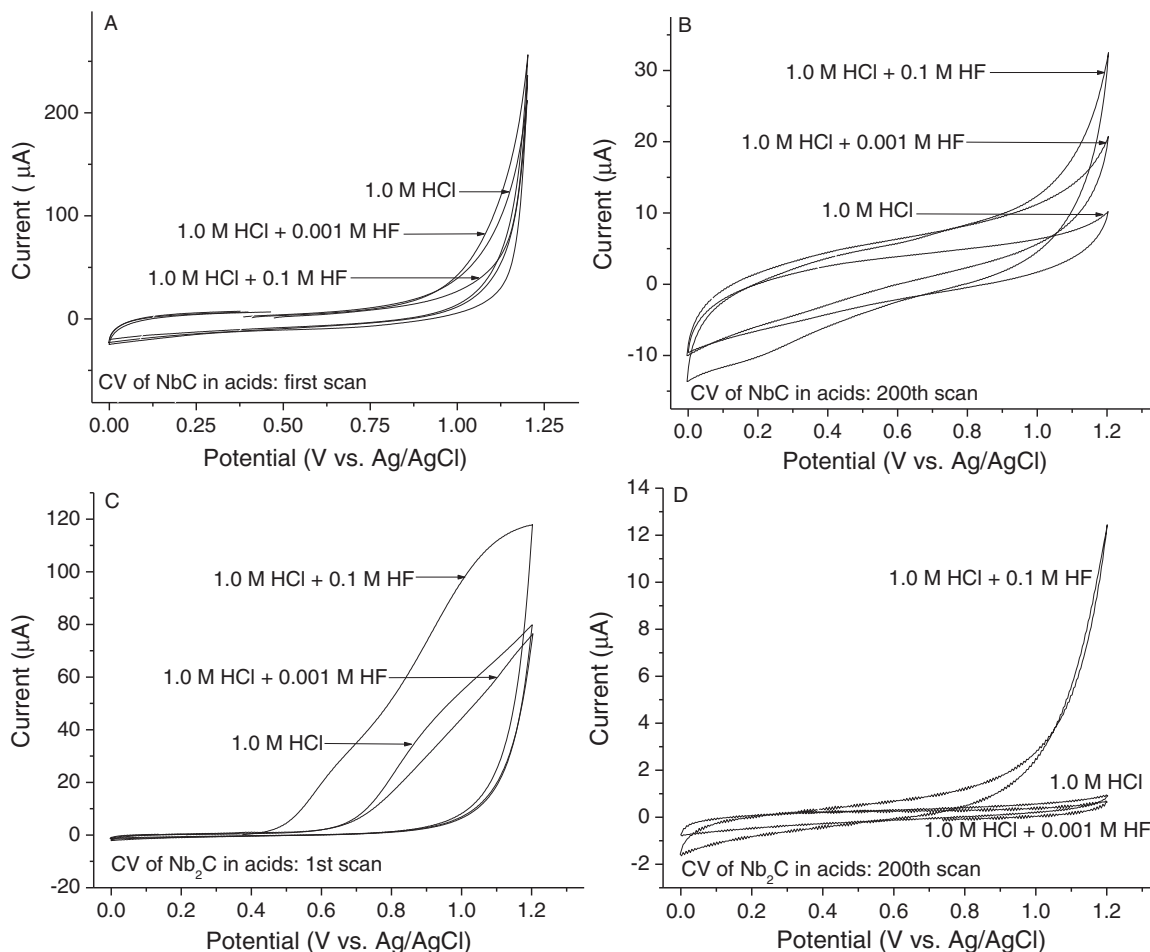


Figure 3. CVs for NbC and Nb₂C electrodes in 1.0 M HCl solutions contain 0.001 M HF and 0.1 M HF, respectively. The scan rate was 0.1 V/s. (A) NbC, the first scans; (B) NbC, the 200th scans; (C) Nb₂C, the first scans; (D) Nb₂C, the 200th scans.

and 0.1 M HF, the electrolyte solution has the highest Nb concentration after 200 scans, which agreed with the higher residual current observed in Figures 3B and 3D. Although Nb₂C showed lower oxidation potentials and larger initial oxidation currents, compared with NbC (Figure 2), the total Nb in the electrolyte solution after oxidation of Nb₂C is lower (Table I). This may indicate that only the top several layers of Nb in Nb₂C can be oxidized and dissolved into the solution; while the oxidation of NbC can go deeper into the material matrix.

When a mixture of NbC and Nb₂C, as indicated by the relative intensity of XRD peaks associated with the two phases, is oxidized in 1.0 M HCl, the oxidation potential is lower than that of pure NbC and higher than that of Nb₂C as is shown in Figure 4. The oxidation occurred at about 0.7 V, a value that is between the 0.9 V (for NbC) and 0.6 V (for Nb₂C). This result indicates that in the mixed phase samples, Nb₂C, embedded in an NbC matrix may be oxidized first at lower potential than NbC, but not as readily as single phase Nb₂C.

Electrochemical oxidation of tantalum carbides.—Tantalum and niobium are in the same group of the periodic table and have very similar chemical properties. This is also true for their carbides. Niobium

carbides and tantalum carbides also have very similar crystal structures. Both NbC and TaC have a cubic crystal lattice; while Nb₂C and Ta₂C have a hexagonal crystal lattice. Niobium carbides and tantalum carbides can all be converted to CDC by Cl₂ gas at elevated temperatures. However, the electrochemical oxidation of tantalum carbides (TaC and Ta₂C) in aqueous solutions is not significant at a potential as high as 1.2 V vs. Ag/AgCl in KCl, NaOH, HCl, or HCl/HF solutions. The oxidation current is very low (<25 μA) even in the first scan, Figure 5. This small oxidation current could be partially attributed to the decomposition of water. In spite of their similar crystal structures and chemical behaviors, tantalum carbides behave quite differently in the electrolyte solutions investigated in this work. After electrochemical oxidation, the Ta concentration in the electrolyte solutions is not above the background measured in the electrolyte solution before the electrochemical measurement.

Electrochemical oxidation of titanium carbides.—TiC electrodes are very stable in 0.1 M KCl and 0.1 M HCl electrolyte solutions. No significant oxidation is observed in these solutions when the electrode potential is swept to as high as 1.2 V for more than 100 cycles.

Table I. Concentration of Nb detected (ppm) in total one mL of electrolyte solution obtained after cycling the NbC or Nb₂C electrodes (surface area of 0.44 cm²) in different electrolyte solutions for 200 scans.

Electrode \ Solution	0.1 M KCl	1.0M HCl	0.001 M HF + 1.0M HCl	0.01 M HF + 1.0M HCl	0.1 M HF + 1.0M HCl
NbC	0.0050	0.079	0.18	0.35	0.44
Nb ₂ C	0.0026	0.040	0.10	0.19	0.40

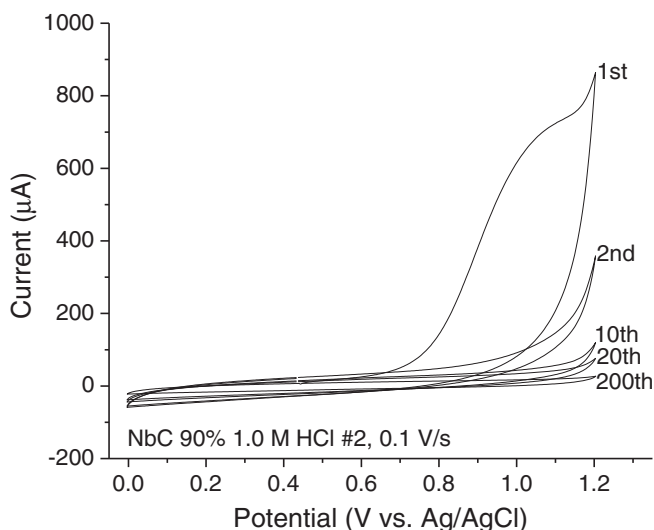


Figure 4. CVs obtained with mixtures of NbC and Nb₂C: 90% NbC and 10% Nb₂C as measured by the relative intensity of the XRD peaks.

However, when HF is added into the acidic electrolyte solution, TiC can be easily oxidized at a potential of 0.4 V or higher. Figures 6A and 6B show the CVs of TiC oxidation in 0.1 M HCl / 0.1 M HF equal-volume mixture. In contrast with all of the other metal carbide electrodes, an oxidation peak at approximately 0.9 V appeared. The absence of a re-deposition peak when the electrode potential is reversed indicates that the oxidation of the coating is completely irreversible. The oxidation peak current (at 0.9 V) increased, probably due to larger surface area after oxidation and removal of Ti, within the first several cycles and reaches a maximum value after approximately 10 scans. Then, the peak current decreased gradually until the 100th cycle, probably due to a smaller amount of Ti available for reaction. The larger specific surface area is also reflected by the slightly larger non-Faradic current between 0–0.5 V in Figure 6B. However, when the electrochemical oxidation is done in 0.1 M NaOH solution, we only observed the oxidation in the first positive scan beginning at about 0.1 V. The oxidation currents dropped to a very low value in the successive scans. There is no significant color change after the oxidation in NaOH. Meanwhile, a tiny reduction peak at ~0.02 V can be seen which may indicate a thin layer of redox active titanium compound

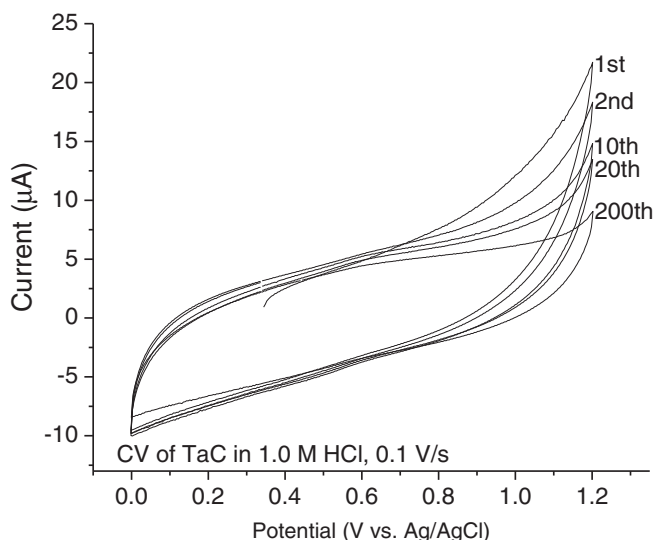


Figure 5. CVs of TaC in 1.0 M HCl at scan rate of 0.1 V/s, 1st to 200th scans.

formed on the electrode surface. In KCl solution, the electrochemical behavior is similar to that in the NaOH solution; the oxidation is only observed in the first cycle, Figure 6D. In both basic (NaOH) and neutral (KCl) solutions, the faradaic current in the first scan is very low—less than 17 μ A.

Electrochemical oxidation of titanium chromium carbides.—Oxidation of TiCrC starts at about 0.5 V in either 0.1 M HCl or 0.1 M HCl/0.1 M HF solutions as shown in Figure 7. An oxidation peak can be observed at ~0.9 V over the first several scans but disappeared in the successive scans when the oxidation appears to reach a limit. The non-Faradic current between 0–0.5 V continues to increase indicating a larger surface area. In NaOH solution, the oxidation started at approximately 0.3 V and also showed an oxidation peak at about 0.9 V.

Electrochemical oxidation of vanadium chromium carbides.—V₂C and VC can be oxidized at about 0.4–0.5 V in a neutral (KCl) solution; while in acidic solutions, the oxidation potential is slightly higher.¹⁶ When the ternary metal carbide VCrC is tested in aqueous solutions, it can also be oxidized at about 0.4 V in 0.1 M KCl and at 0.5 V in 0.1 M HCl as shown in Figure 8. In both solutions, both vanadium and chromium can be detected after the oxidation, indicating that both vanadium and chromium are oxidized and dissolved in the solutions. The oxidation current (Faraday current) at higher potential decreased gradually as multiple scans are performed. The solid electrode material is eliminated gradually from the surface as the number of scans increase. Eventually, the entire VCrC layer is removed from the substrate after about 20 scans (depending on the thickness of the layer and the composition of the electrolyte solution).

In summary, we have attempted to electrochemically oxidize several metal carbides. The Ta-containing carbides, TaC and Ta₂C, were not readily oxidized in the solutions tested. The electrolyte solutions were collected and diluted by 5% nitric acid and then the metal contents in the solutions were measured by ICP-MS. Metals including Nb, V, Cr, or Ti can be detected in the electrolyte solutions after electrochemical oxidation. However, a Ta content above background cannot be detected for any electrolyte solution after electrochemical cycling. When TiCrC is oxidized, in all the solutions used as electrolytes, both Cr and Ti can be detected after the electrochemical oxidation, indicating that neither Cr nor Ti is selectively oxidized. The highest metal concentrations of each one are obtained in HCl/HF solution, while the lowest concentrations are obtained in NaOH.

The oxidation potentials are listed in Table II. The elements Ta, Nb, and V are in the same group (4B) of the periodic table. The oxidation of their carbides can be ranked, from hard to easy, as tantalum carbides, niobium carbides, and vanadium carbides mimicking their rankings in atomic and ion sizes. The size of the metal ions might be critical to determine the thermodynamics of the ions being “extracted” into the electrolyte solution after electrons are removed from the electrodes. The elements of Ti, V, and Cr are neighbor elements in the same period. TiC is one of the most stable, hard, and refractory materials. In an acidic solution, TiC can only be oxidized when HF is added. In basic solution, TiC is oxidized at a more positive potential, compared to other carbides in NaOH solution. On the other hand, TiCrC, VC, and VCrC can be oxidized at relatively lower potentials in acidic, neutral, or basic solutions, compared with other carbides. The synthesis of analogous chromium carbides (CrC or Cr₂C) is not straightforward, therefore, the electrochemical oxidation of chromium carbides was not investigated in this work.

Characterization of the post-oxidation electrode.—After multiple scans of electrochemical oxidation, the electrode surface was characterized by Raman spectroscopy and imaged using SEM. As shown in Figure 9, the spectra obtained from the NbC, TiC, and TiCrC electrodes show the typical “D-band”, ~1360 cm⁻¹, and “G-band”, ~1590 cm⁻¹ that have been assigned to the CDC and indicate the existence of a mixture of sp³ and sp² hybridized carbon atoms. This agreed with the results and conclusions of electrochemical measurements of VC and

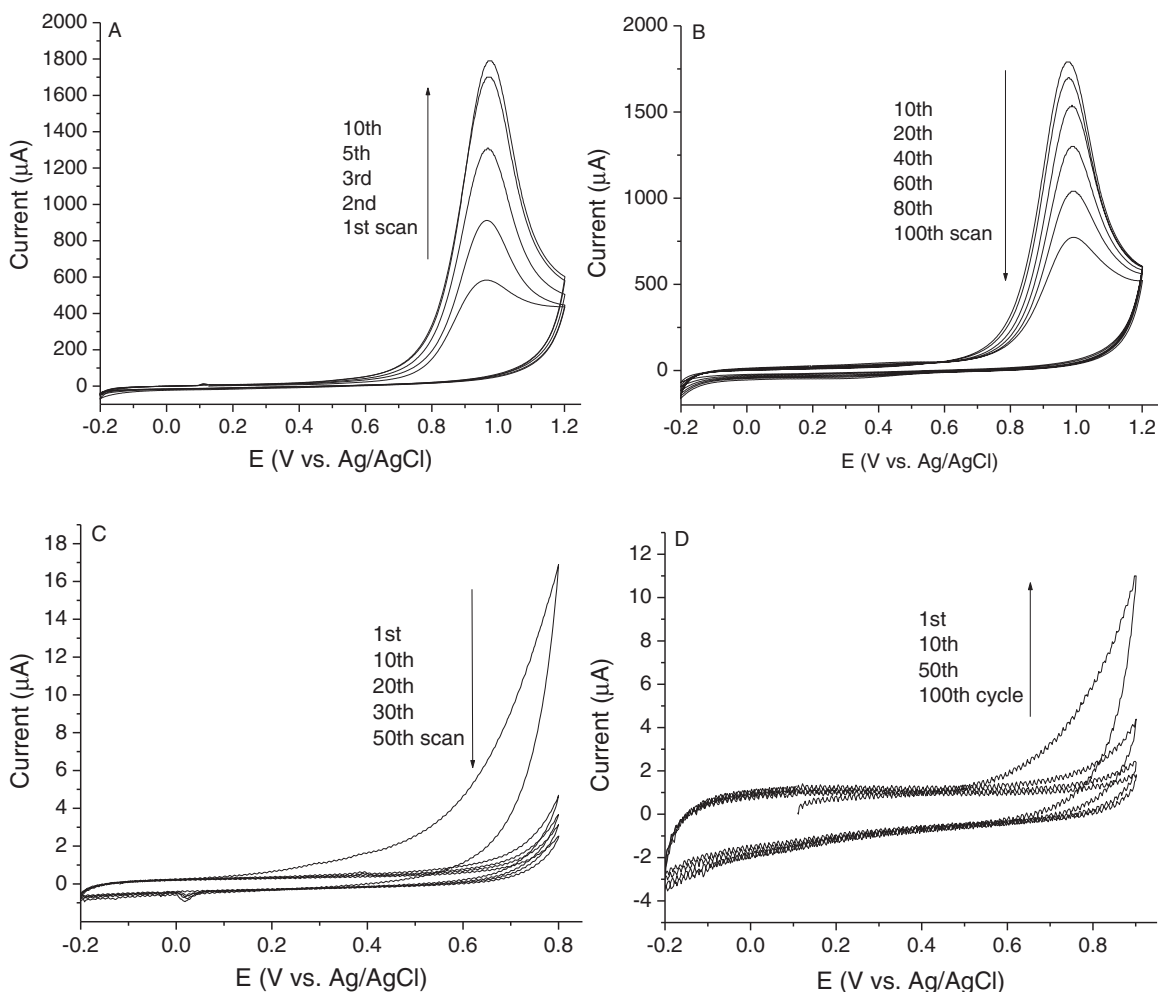


Figure 6. The CV of TiC in 1:1 mixture of 0.1M HF/0.1M HCl solution: (A) 1st-10th scans; (B) 10th-100th scans. (C) CVs of TiC in 0.1 M NaOH. (D) CVs of TiC in 0.1 M KCl. Scan rate = 0.1 V/s.

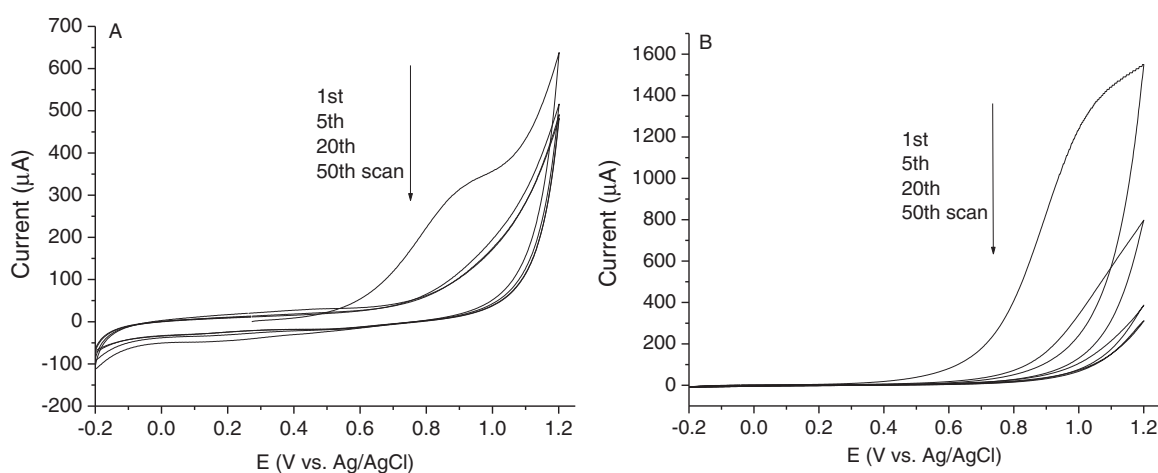


Figure 7. CVs of TiCrC in 0.1 M HCl (A), and in 0.1 M NaOH (B) electrolyte solution. Scan rate = 0.1 V/s.

Table II. Critical potential of the electrochemical oxidation of the metal carbides referenced by Ag/AgCl electrode at a scan rate of 0.1 V/s.

	NbC	Nb ₂ C	VC	VCrC	TiC	TiCrC
HCl or HCl/HF	0.9 V	0.6 V	0.6 V	0.3 V	0.6 V	0.5 V
KCl	0.7 V	0.4 V	0.5 V	0.3 V	0.6 V	0.6 V
NaOH	0.3 V	0.2 V	-0.4 V	-0.2 V	0.1 V	0.3 V

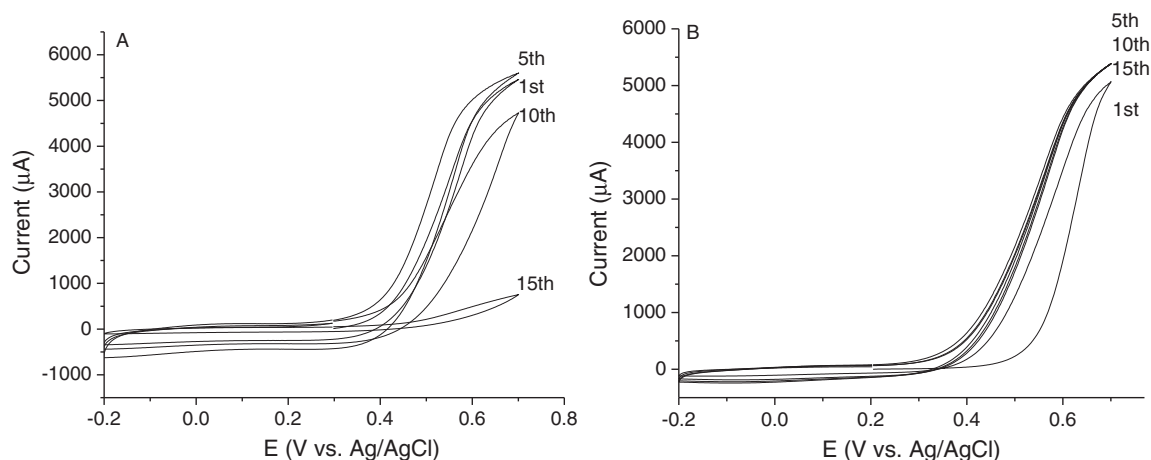


Figure 8. The CVs of VCrC in 0.1M KCl (A), and 0.1M HCl (B) electrolyte solution at a scan rate of 0.1 V/s.

V₂C in a previous publication.¹⁶ In these systems, surface layers of metal are removed by oxidation and the “extra” carbon that remained on the surface formed porous CDC. The two Raman scattering bands are not observable when TaC or Ta₂C electrodes are oxidized in any of the electrolyte solutions used in this study. Nb₂C can be oxidized based on the electrochemical and ICP-MS results, but the two scattering peaks were not observed in the Raman spectrum after oxidation, probably because the carbon layer is too thin or comes off the electrode. In addition, after electrochemical oxidation, the VCrC coating is completely removed from the substrate with no carbon remaining for the Raman measurement.

All the metal carbides have a shiny dark gray appearance before the electrochemical oxidation. After the oxidation, the surface changed to a matte black (in the cases of NbC, Nb₂C, VC, VCrC, TiCrC, and TiC in HCl/HF) or navy blue (in the case of TiC in NaOH) appearance. When etching of a TaC or Ta₂C coating was attempted, no surface color / shade changes was observed after the reaction. The surface morphology of the post-oxidation electrodes are characterized by SEM imaging with results shown in Figure 10. When NbC or Nb₂C is oxidized, the morphology has no significant change before and after the electrochemical oxidation in the electrolyte solutions investigated as shown in Figures 10A and 10B. VCrC shows hexagonal crystal domains before electrochemical oxidation. The etching may first happen at the interfaces of the crystal grains and then finger-like morphologies can be observed after the oxidation (Figures 10C and 10D). Both TiC and VC have cubic crystal structure before the oxidation (Figures

10E and 10G). After the electrochemical oxidation, the crystal structures have been destroyed by removal of the metal atoms from the lattices. Porous (from TiC) or “Karst” topography (from VC) CDC is left over on the electrode surface shown in Figures 10F and 10H. The TiCrC coating produced porous CDC after electrochemical etching in an acidic solution as shown in Figure 10J, or CDC with cracks after electrochemical etching in basic solution as shown in Figure 10K.

Conclusions

Transition metal carbides have unique chemical and physical properties such as chemical inertness, similarities in valence orbitals to those of Pd, Ni, or Rh catalytic metals, high hardness, high melting temperatures, and high thermal conductivity. These properties can be exploited for applications in many areas of the chemical and mechanical industries. Due to their chemical stability and poor sintering ability, research on the chemical properties of metal carbides is limited. In this paper, we investigate the electrochemical properties of VC, NbC, Nb₂C, TaC, Ta₂C, TiC, TiCrC, and VCrC coatings in aqueous electrolyte solutions with the presence of HCl, NaOH, and HF. Cyclic voltammetry and elemental analysis demonstrate that both the cubic and hexagonal metal carbides can be oxidized electrochemically at a “mild” electrode potential (<1.0 V vs. Ag/AgCl in all the cases) producing soluble metal ions in the solutions. The carbon remaining on the surface of the electrode after oxidation is sp³ or sp² hybridized, resembling the structure of CDC as synthesized by the chlorination

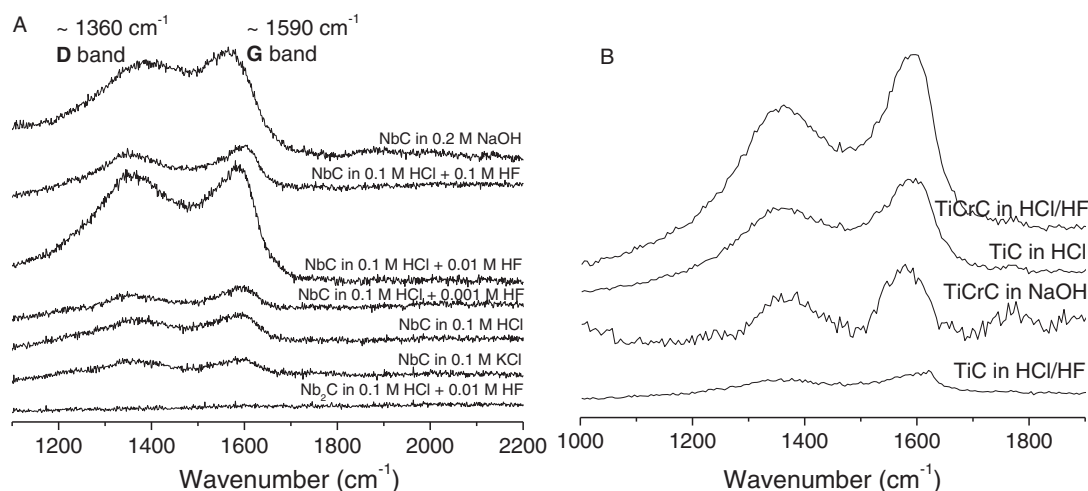


Figure 9. Raman spectra of (A) NbC and Nb₂C substrates and (B) TiC and TiCrC substrates after electrochemical oxidation.

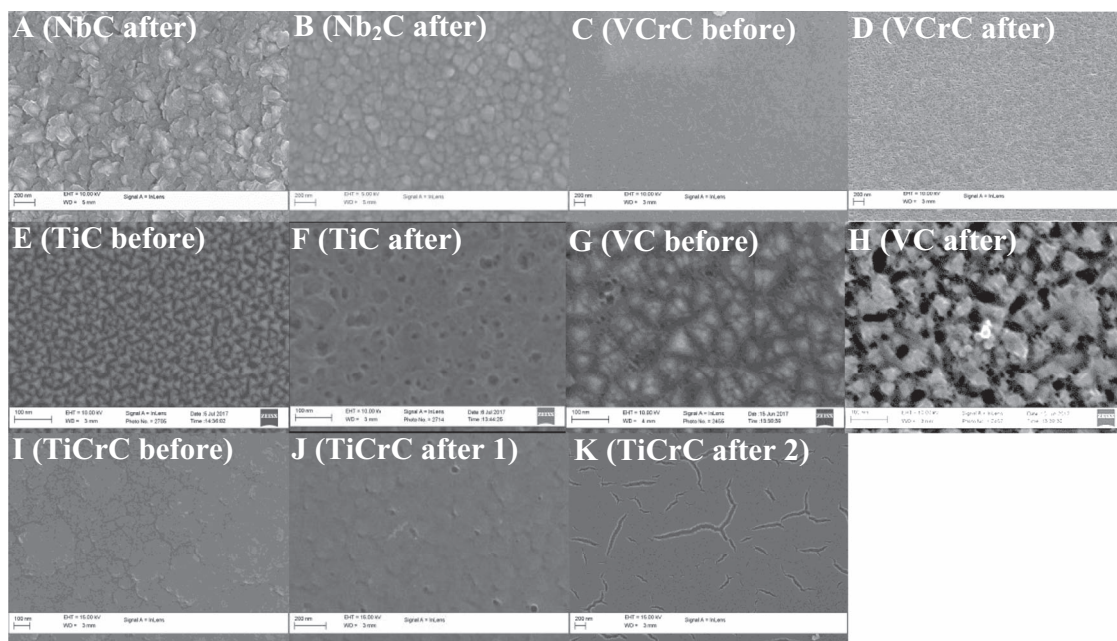


Figure 10. SEM images of NbC electrode in KCl/HF (A), Nb₂C electrode in HCl/HF (B), VCrC electrode before oxidation (C), VCrC electrode after oxidation in HCl (D), TiC electrode before oxidation in HCl/HF (E), TiC electrode after oxidation in HCl/HF (F), VC electrode before oxidation (G), VC electrode after oxidation in HCl (H), TiCrC electrode before oxidation (I), TiCrC electrode after oxidation in HCl/HF (J), and TiCrC electrode after oxidation in NaOH (K).

method. SEM images demonstrate that the surface morphology of the NbC and Nb₂C electrodes has no significant change before and after the electrochemical oxidation, indicating that only the niobium metal in the surface layers of the NbC or Nb₂C electrode is oxidized and dissolved in the electrolyte solutions. In contrast, tantalum carbides cannot be oxidized under the same conditions in these aqueous solutions, even though they (niobium carbides and tantalum carbides) have very similar structures as well as chemical and mechanical properties. When VC, VCrC, TiC, and TiCrC electrodes were oxidized, all the resulting CDC porous films have a larger specific surface area in comparison with the precursor films.

Acknowledgments

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